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Remote Fourier Transform Infrared Air Pollution Studies

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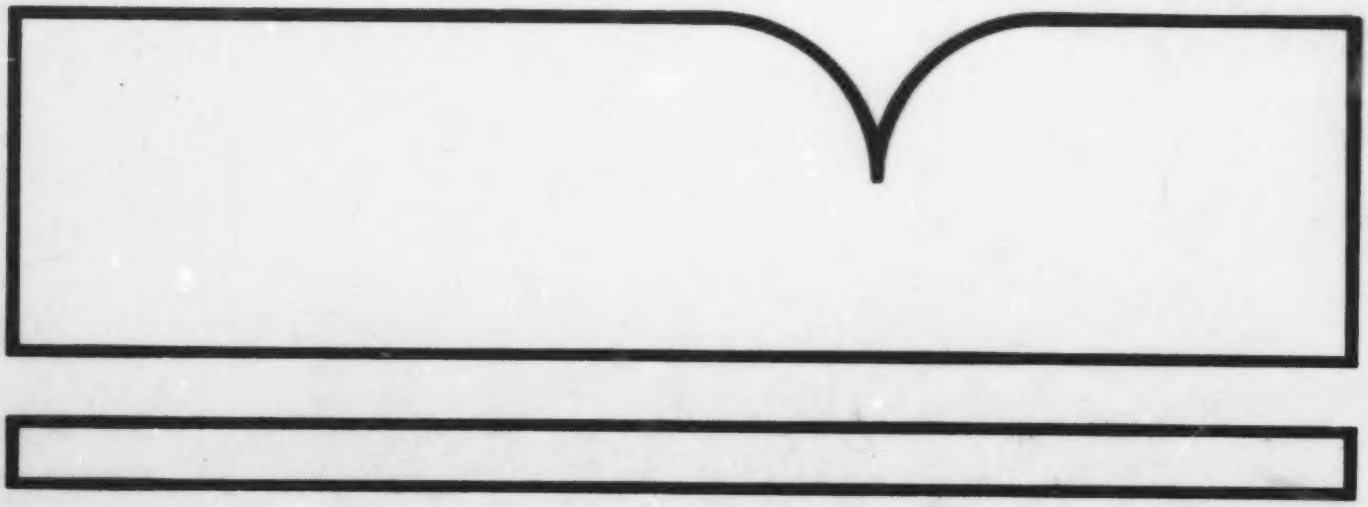

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16. ABSTRACT

A commerical Fourier transform infrared interferometer system has been installed in a van and used to make longpath absorption and single-ended emission measurements of gaseous pollutant concentrations at a variety of pollutant sources. The interferometer system is described and results of recent emission measurements of a jet engine, brick kiln, gypsum pond, and industrail stacks are presented. The system covers the infrared spectral region from 650 to 6000 cm^{-1} at a maximum resolution of 0.06 cm^{-1}. In the absorption mode, many gaseous pollutants can be detected at parts-per-billion levels over a one-kilometer path. In the emission mode, warm gases exiting industrial stacks can be detected at parts-per-million levels. The temperature of the stack gases can be determined directly from the spectra. In the jet engine measurements, acetelyne, ethylene, and formaldehyde (among others) were observed; H_2SO_4, SO_2, HF and HCl were among the species seen at the brick kiln; and remotely determined temperatures were within ten percent of instack values.

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*Gases		07D
*Remote sensing		14B
Measuring instruments		20F
*Optical interferometers		15E
Mobile equipment		

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Remote Fourier transform infrared air pollution studies

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Abstract. A commercial Fourier transform interferometer system has been installed in a van and used to make long-path absorption and single-ended emission measurements of gaseous pollutant concentrations at a variety of pollutant sources. The system covers the infrared spectral region from 650 to 6000 cm^{-1} at a maximum resolution of 0.06 cm^{-1}. In the absorption mode, many gaseous pollutants can be detected at parts per billion levels over a one kilometer path. In the emission mode, warm gases exiting industrial stacks can be detected at parts per million levels. The temperature of the stack gases can be determined directly from the spectra. This paper describes the interferometer system and results of recent measurements of jet engine, brick kiln, gypsum pond, and industrial stack emissions.

Keywords: remote sensing; Fourier transform spectroscopy; air pollution measurements; infrared systems.

Optical Engineering 19(4), 508-514 (July/August 1980)

I. INTRODUCTION

The use of longpath, high resolution infrared spectroscopy for analysis of gaseous air pollutants extends over the past 25 years. These measurements, which include those made in the open atmosphere and in multiple-pass cells, have been reviewed by Hanst.[1,2] Essentially all of the systems described by Hanst were stationary systems. The use of a Fourier transform interferometer as part of a mobile system was pioneered by Block Engineering with the measurements being carried out primarily on military targets. The first extensive use of a mobile Fourier transform infrared (FT-IR) system for air pollution measurements was conducted by General Dynamics/Pomona in 1971.[3] In both of these FT-IR systems, interferograms collected in the field were returned to a central computer for processing. In 1972, the Environmental Protection Agency (EPA) received a mobile spectrometer system called the ROSE (Remote Optical Sensing of Emissions) System that utilized a grating monochromator. This system did not have sufficient spectral resolution to detect trace amounts of pollutant species. In 1977, the grating monochromator and its associated components were replaced with a commercial FT-IR system so as to provide the necessary spectral resolution along with an essentially real-time data processing capability in the field.[4,5]

The ROSE system is used in two modes: (1) with a remotely located light source to make longpath (up to 1.5 kilometers) absorption measurements, and (2) with an adjustable tracking mirror to make single-ended emission measurements of stack effluents. The major purpose of these types of measurements is to characterize (determine species identity and concentration) the gaseous pollutants emitted to the atmosphere from both point and extended area sources. The particular advantages of the mobile spectrometer system over other methods are that no samples need be collected and that there need be no prior knowledge of the identity of the pollutants. (Almost all major pollutant gases possess an infrared spectral signature, although for some species the ultraviolet spectral region affords greater sensitivity.) The measurements made during the first year of the use of the ROSE system were presented in Ref. 4. Presented here are the results of some recent measurements along with a description of the spectrometer system and its operating characteristics.

II. THE ROSE FT-IR SYSTEM

A schematic of the ROSE optical system is shown in Fig. 1, and the arrangement of the system in the ROSE van is shown in Fig. 2. The light source-telescope system used for the longpath absorption measurements is shown in Fig. 3. The f/5 scope is of Dall-Kirkham configuration with a 30 cm diameter primary mirror. The light source is a 1000 watt quartz-halogen lamp. This lamp provides considerably more near-infrared energy than a 1500 K blackbody previously used and in wavelength regions where the quartz envelope is opaque, its thermal emission is about equal to that of the blackbody. In addition, the intense visible energy from this source aids system alignment. All system components are carried to the measurement site in the single van. At the site, the light source-telescope is usually moved into the back of a rented pickup truck and driven to a desired location; a small generator powers the light source if local power is not available.

The receiver telescope (identical to that described above) collects energy from the remote light source directly through a port in the side of

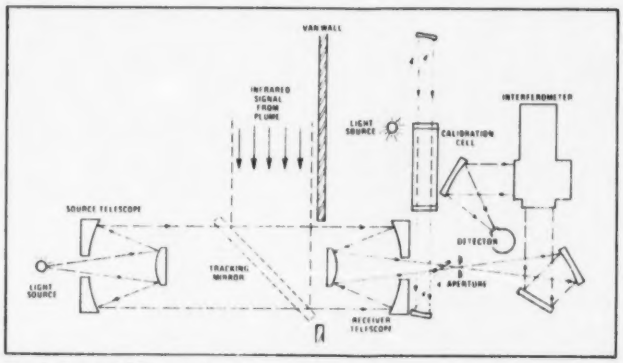

Fig. 1. The ROSE optical system.

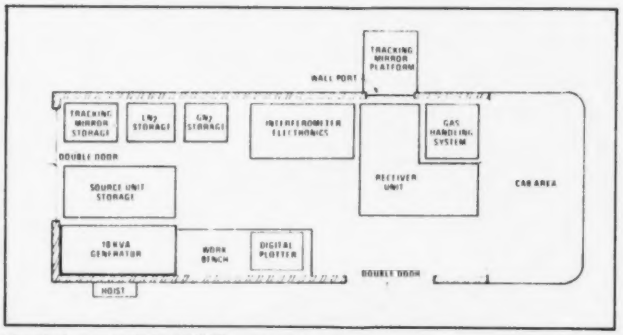

Fig. 2. Layout of the ROSE system in van.

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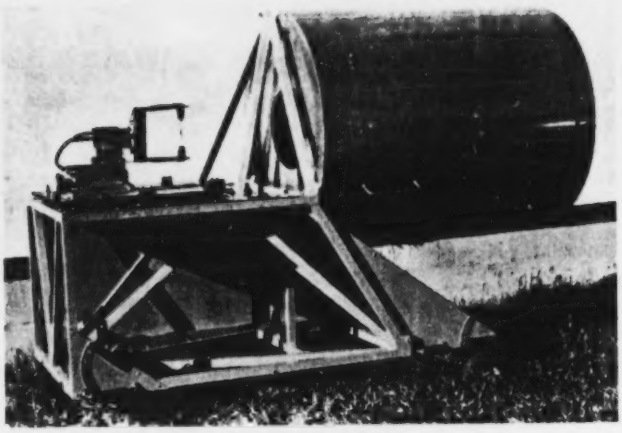

Fig. 3. The ROSE system light source-telescope.

the van, as indicated in Fig. 1. To measure the infrared signal from warm stack effluents, an elliptically shaped flat mirror (called the tracking mirror in Fig. 1) reflects energy through the port into the telescope. The tracking mirror is mounted on a platform attached to the side of the van (Fig. 4). The receiver telescope focuses energy (in either mode of operation) at the interferometer aperture, which is adjustable in size for compatibility with desired spectral resolution. The interferometer and peripheral equipment comprise a standard Nicolet Instrument Corporation Model 7199 FT-IR system configured to fit into the van. Major components of this system consist of a computer with 40K memory, dual-density disk drive with 4.8 million 20-bit word capacity, teletype keyboard, paper tape reader, oscilloscope interactive display unit, and a high-speed digital plotter. The major components of the interferometer system are shown in Fig. 5.

The detector is of a dual-element sandwich-type configuration mounted in a liquid nitrogen dewar. For the 1800 to 6000 cm^{-1} region InSb is used, and HgCdTe is used from 600 to 1800 cm^{-1}; the regions are scanned separately. The InSb detector, which is transparent in the longer wavelength region, is mounted immediately in front of the

Fig. 4. The ROSE system tracking mirror.

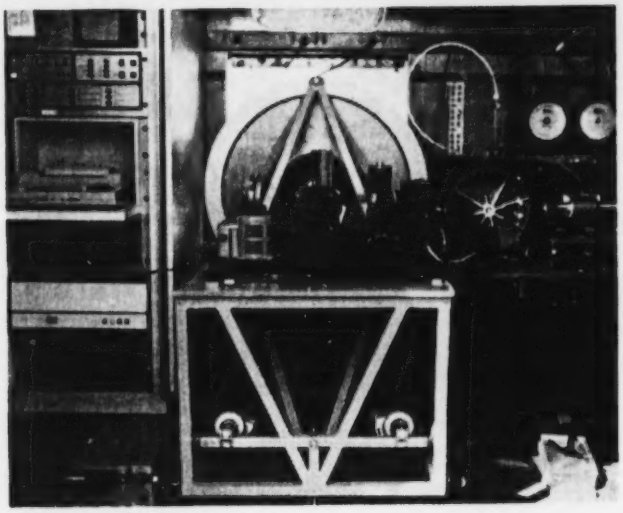

Fig. 5. The ROSE system.

HgCdTe detector. Detector selection is achieved by a keyboard command. Two beamsplitters are used with the interferometer: BaF_2 from 900 to 6000 cm^{-1} and ZnSe from 650 to 900 cm^{-1}. Figures 6 and 7 compare the spectral transmission characteristics of the two beamsplitters. ZnSe is used instead of NaCl or KBr because it is nonhygroscopic. A beamsplitter interchange and realignment takes about five minutes.

In the longpath absorption mode, initial alignment of the telescopes is achieved by visually boresighting each at the other. Final alignment is

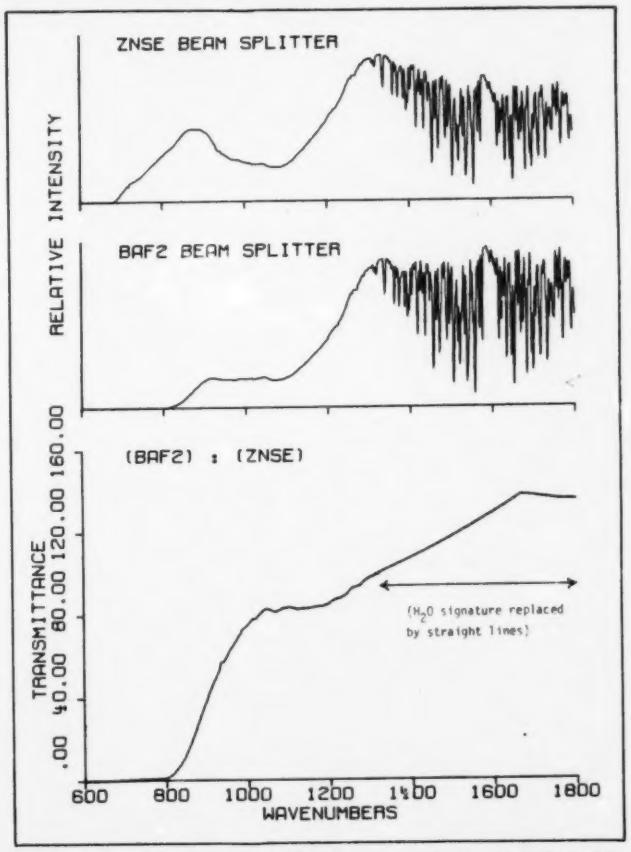

Fig. 6. Comparison on ZnSe and BaF_2 beamsplitters over the 600 to 1800 cm^{-1} region.

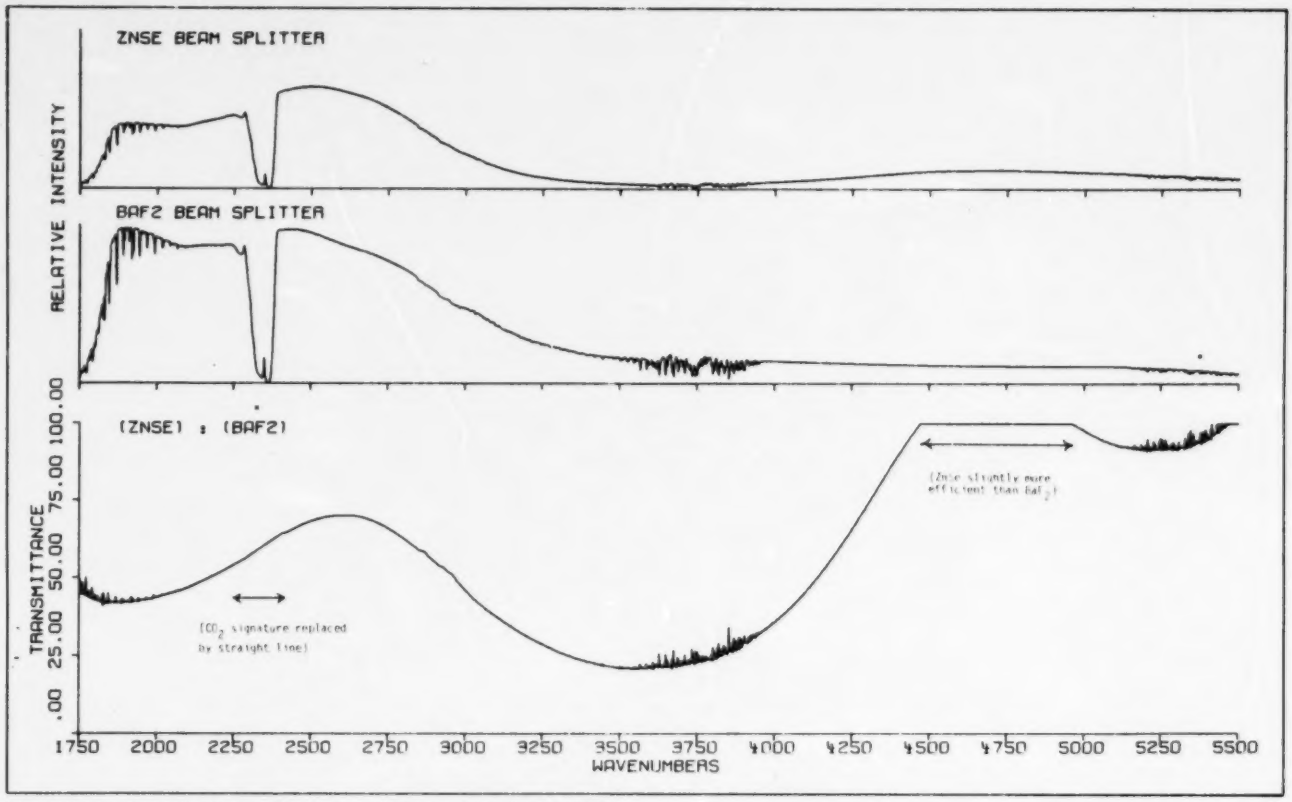
ZNSE BEAM SPLITTER
BAF2 BEAM SPLITTER
RELATIVE INTENSITY
(ZNSE) : (BAF2)
TRANSMITTANCE
.00 25.00 50.00 75.00 100.00
(CO2 signature replaced by straight line)
(Znse slightly more efficient than BaF2)
1750 2000 2250 2500 2750 3000 3250 3500 3750 4000 4250 4500 4750 5000 5250 5500
WAVENUMBERS

Fig. 7. Comparison of ZnSe and BaF_2 beamsplitters over the 1800 to 5500 cm^{-1} region.

made by maximizing source signal level at the interferometer aperture with the assistance of two-way radios. For stack emission measurements, alignment using the tracking mirror is achieved by boresighting and by observing the image projected by the telescope at the interferometer aperture. The tracking mirror can be adjusted manually from inside the van about the telescope axis and a vertical axis. This alignment system is sufficiently precise to allow manual tracking of the sun for solar absorption measurements. The interferometer base plate is supported at one end by the telescope support structure and by an adjustable support at the other end. Once the van has been positioned and the telescope aligned, the interferometer is leveled using the adjustable support. A flat turning mirror (next to the aperture in Fig. 1) is then adjusted to insure that light entering the interferometer returns upon itself to the aperture (this is done with the beamsplitter removed). The interferometer is then ready for final alignment.

Auxiliary equipment carried in the van includes a weather station for recording wind velocity and temperature and a laser range-finder for measuring path lengths. For stability in the longpath configuration, four jacks are lowered from the van chassis to the ground. Power for the ROSE system, including that needed for heating or air conditioning, is supplied by a 10 kw generator. Prior to final positioning of the van, the generator is lowered to the ground using an electrically operated winch. This procedure is necessary to avoid electrical and mechanical interference with the operation of the interferometer. During transportation of the van to a field site, two precautions are observed: the beamsplitter is removed from the interferometer and the disk drive head is clamped back away from the disk. An initial setup of the entire system requires two to three hours (about one hour for an emission measurement). Subsequent setups in the same vicinity require about one hour under normal conditions.

The ROSE system has been on about a dozen field trips since installation of the FT-IR system. No optical problems have been encountered due to vibrations inherent to traveling (the interferometer can be realigned in a matter of minutes after reinsertion of the beamsplitter). One minor problem has occurred after system setup—on initial data collections the teletype indicated erroneous error messages. This problem has always been corrected by reseating circuit boards in the computer and verifying the integrity of all intercomponent cable connections.

The ROSE system has been used in several configurations that vary somewhat from the basic modes described above: (1) by utilizing platforms and an additional elliptical flat, it was possible to obtain a horizontal optical path across large elevated sources (the additional flat reflected the light beam down to the van at ground level); (2) by utilizing a small telescope and several turning mirrors, it was possible to transmit energy through ports in an industrial stack and down to the ROSE van and thus obtain direct absorption measurements of the stack gases; and (3) ultralongpath measurements have been made using the sun or the moon as a light source. For analysis of collected gas samples or of calibration gases, the minimum detectable concentrations have been limited to about 1 ppm by the maximum available cell length of 1 meter; it is planned to add a multiple-pass cell to the ROSE system that will provide path lengths in excess of 100 meters. Also, a cell that can be heated to 1000 K will be added to the system.

III. SYSTEM CALIBRATION

The calibration of ROSE system spectra from longpath measurements follows the conventional procedure of obtaining the spectra of known concentrations of desired species (broadened to atmospheric pressure) contained in a sample cell (shown in Fig. 1). The calibrations are made after the field trip in order to match instrument resolution and sample optical depth with field measurement conditions. A vacuum transfer system with appropriate gauges is used in filling the cell to desired pressures. Cells ranging in length from 1 to 100 cm are available.

Emission spectra are calibrated in terms of spectral radiance by comparison with the spectrum of a blackbody radiation source at known temperature. All the necessary calculations, including that of the

Planck function, are carried out with standard system software. If the absorption coefficients of the observed gases are known (from the literature) as a function of temperature, then their concentrations can be calculated.

In cases where CO_2 is a major combustion product in stack effluent (e.g., a coal-burning power plant), it has been found possible to reliably determine the stack gas exit temperature from the emission spectrum of the ν_3–ν_1 CO_2 band at 960 cm^{-1}. In these cases, the calculations are simplified by the fact that within a stack diameter of the top of the stack, temperature and concentration gradients are minimal.

The equations pertinent to the three calibration procedures are given below. The amount of energy transmitted by a gas sample at a given wave number is related to the gas concentration by Beer's Law:

$\tau(\nu) = e^{-K(\nu,T)CL}$ = transmittance at frequency ν (cm^{-1})
$K(\nu,T)$ = spectral absorption coefficient
C = gas concentration (ppm or molecules/cm^3)
L = path length (meters)
T = gas temperature (degrees Kelvin).

The spectral radiance of a gas sample is given by

$$N_G(\nu) = \epsilon(\nu) N_{BB}(\nu,T_G) \text{ [watts cm}^{-2} \text{ steradian}^{-1} (\text{cm}^{-1})^{-1}]$$

$\epsilon(\nu) = 1 - \tau(\nu)$ = gas emissivity

$N_{BB}(\nu,T_G)$ = spectral radiance of a blackbody at the temperature of the gas T_G.

The relative intensities of the lines in the P and R branches of the CO_2 emission spectrum were used to calculate a least squares fit to an equation of the form $Y = AX + B$, where

$$Y = \ln[J\nu_o^4(\gamma N_o)^{-1}]$$

and $J = J' + 1$ for the P branch and $J = J'$ for the R branch.

$X = J'(J' + 1)$
$A = h^2(2\pi)^{-2}(2IkT)^{-1}$
I = moment of inertia of the molecule (in upper state J') about an axis perpendicular to the intermolecular axis and through the molecular center of mass
B = a quantity independent of J'
N_o = spectral radiance at line center ν_o
γ = line half-width at $N_o/2$
k = Boltzmann's constant.

These expressions for gas temperature were developed from Refs. 6 and 7 for a linear rigid rotator.

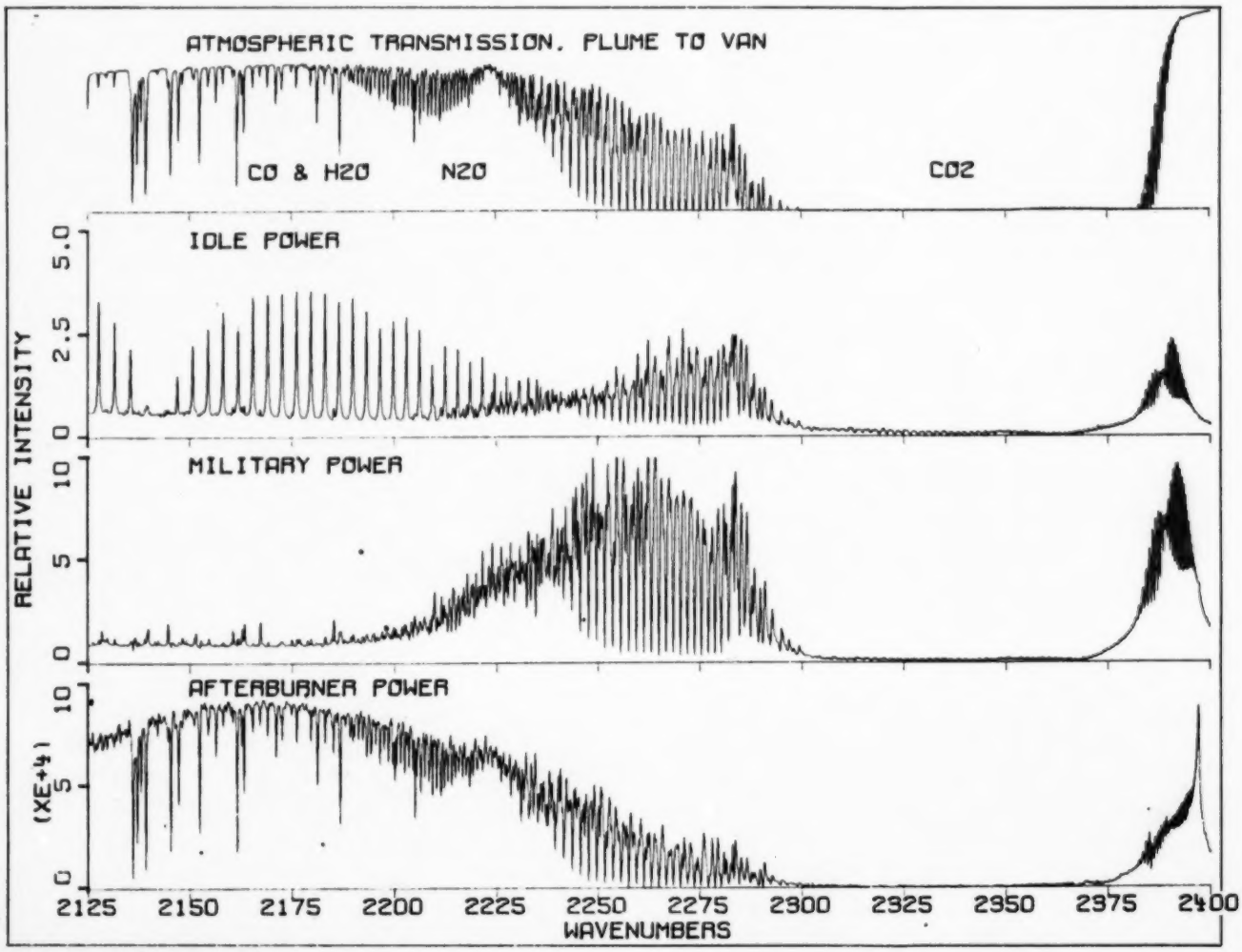

Fig. 8. Jet engine emission spectra.

IV. RESULTS

Recent measurements have been made of emissions from jet engines and brick kilns. Also, past data on emissions from industrial stacks[5] have been analyzed to determine plume temperature. The results of these measurements are presented below. (Resolution is 0.125 cm^{-1} in all spectra.)

A. Jet engines.

In the fall of 1977, during the first field program with the ROSE system after installation of the FT-IR system, a series of absorption and emission measurements were made on jet engine plumes at Tyndall Air Force Base, Florida. At idle engine power the species acetylene, ethylene, carbon monoxide, formaldehyde, and hexane equivalent hydrocarbons were measured in absorption, and the results were in reasonable agreement with previous measurements using extractive sampling techniques.[5] During these measurements, it was found that the high noise levels encountered during engine operation at high power levels seriously disrupted the smooth motion of the moving interferometer mirror (the van was located approximately 75 meters from the jet engine). In early 1979, additional measurements were made with the ROSE van approximately 200 meters from the jet engine. At this range, engine noise did not affect interferometer performance; typical emission spectra are shown in Fig. 8.

During the second set of measurements, it was observed that spectra obtained in the absorption mode at the jet engine nozzle exit were excessively noisy. This was finally traced to the fact that since the telescope diameter approximated the nozzle exit diameter, portions of the light beam passed through sharp and fluctuating density gradients at the top and bottom of the plume, which produced significant beam divergence (observable at the aperture). This effect produced an appreciable modulation of the light beam which translated into signal noise. This problem did not exist downstream of the nozzle exit.

B. Brick kilns

There are two large brick manufacturing facilities near Chicago in which large kilns, approximately 30 meters long × 15 meters wide × 6 meters high and holding 1.5×10^6 bricks, are heated over several days by natural gas. The logistics of the heating procedure allowed placing the ROSE system light source on a completed but unfired kiln and aiming the light beam across the kiln being fired to an elliptical flat placed on a kiln that was in the cooling-down stage, where the beam was then reflected down to the van. The spectra obtained were rich in pollutants as seen in Figs. 9 and 10. Figure 11 shows a portion of a kiln spectrum plotted with the same wavelength scale as used by Burch[8] in his analysis of H_2SO_4 vapor. The shape of the continuum absorption in the kiln spectrum is seen to match that due to H_2SO_4. (There is a difference in the 1100–1200 cm^{-1} region due to the presence of SO_2 in the kiln spectrum.) The concentrations measured and the associated absorption coefficents are given in Table I.

C. Plume temperature measurements

Figure 12 shows emission spectra from the plumes of two types of industrial stacks. Figure 13 shows the temperature plots for the carbon monoxide boiler, and Fig. 14 shows a similar plot for a coal-burning power plant; the spectroscopically determined temperatures were 633 K and 444 K, and in-stack measurements of plume temperatures were 650 K and 425 K, respectively.

D. Gypsum pond measurements

Gypsum ponds are large ($\sim 2.5 \times 10^5 m^2$) waste water treatment ponds at phosphate fertilizer plants. Fluoride has been known for many years to be the primary atmospheric emission from these ponds, and in 1977 ROSE system data showed HF to be species involved.[5] In the summer of 1979, a study was done at a gypsum pond to compare wet chemistry sampling methods with ROSE system data. It was found that with

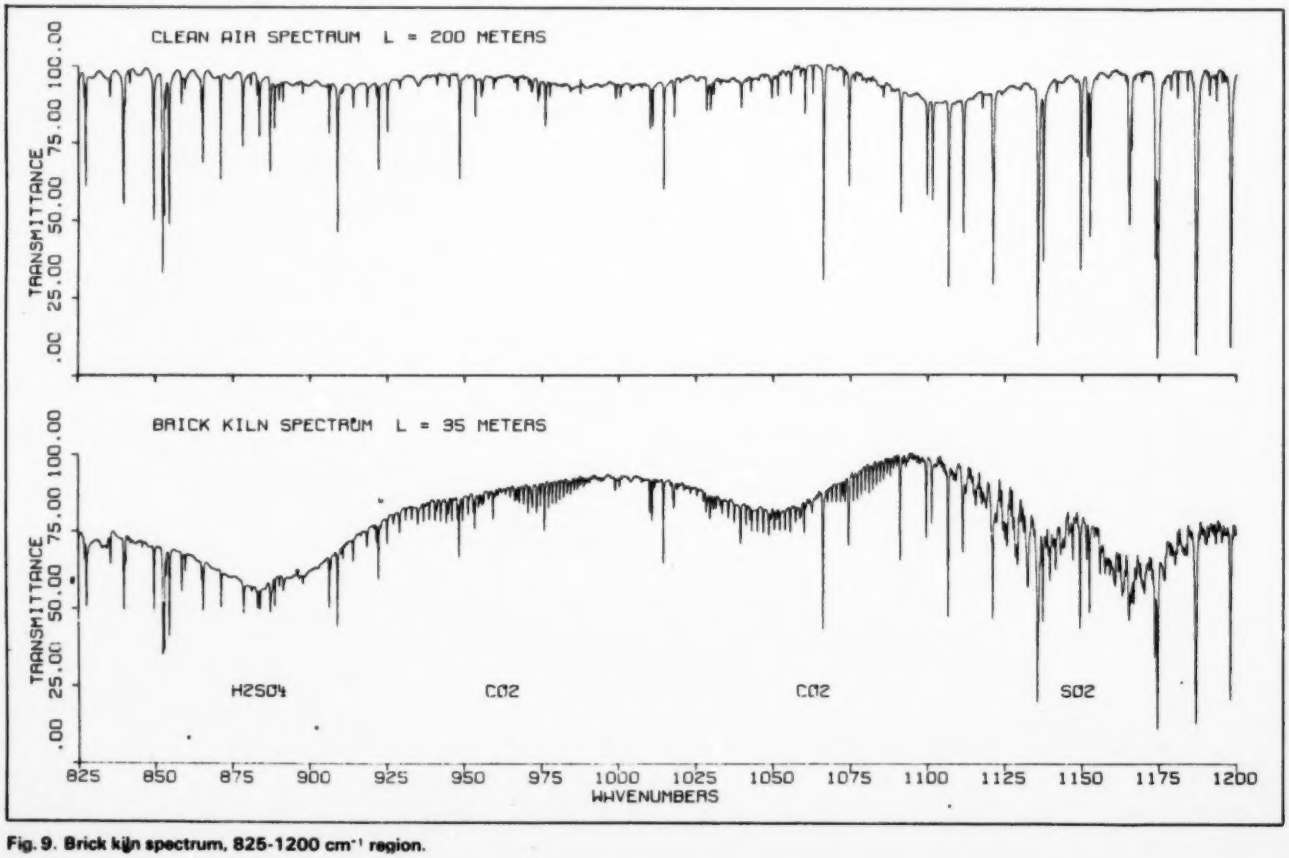

Fig. 9. Brick kiln spectrum, 825-1200 cm^{-1} region.

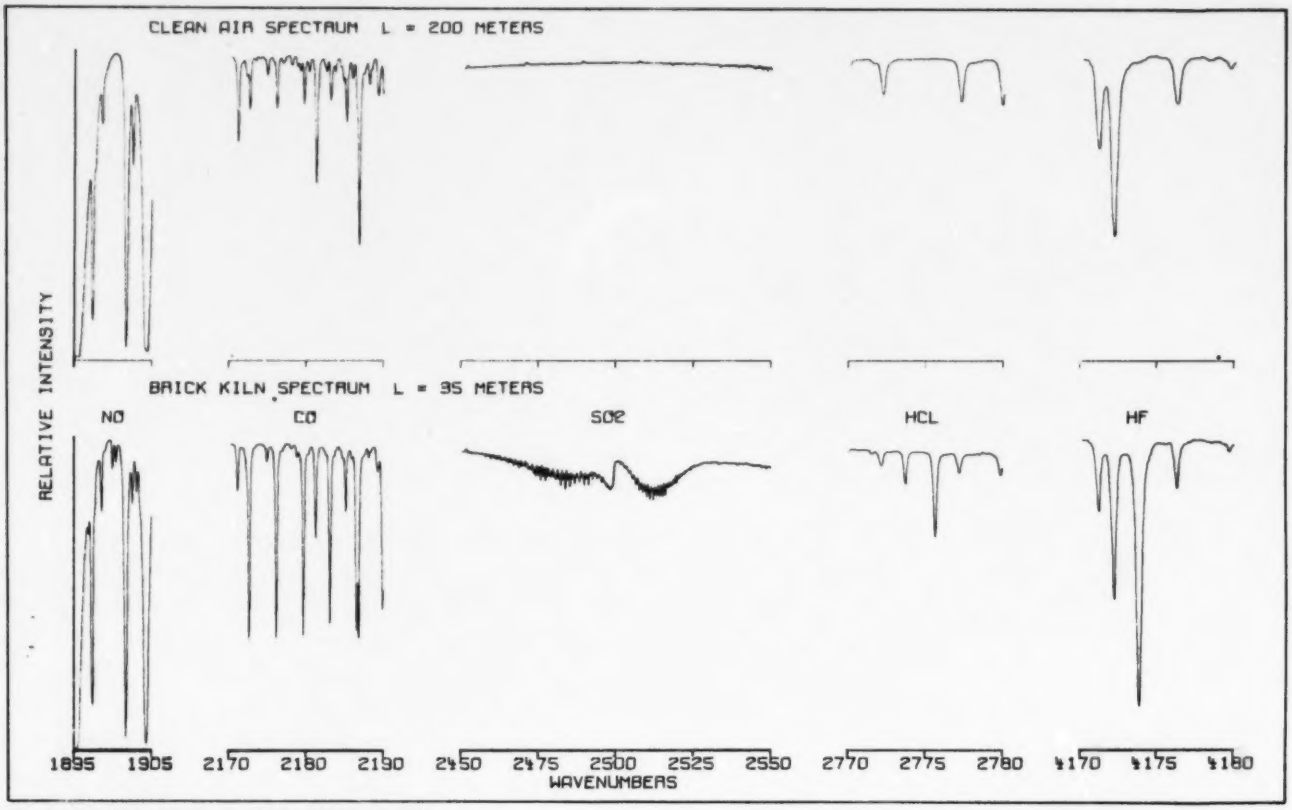

Fig. 10. Brick kiln spectrum, 1800-4200 cm^{-1} region.

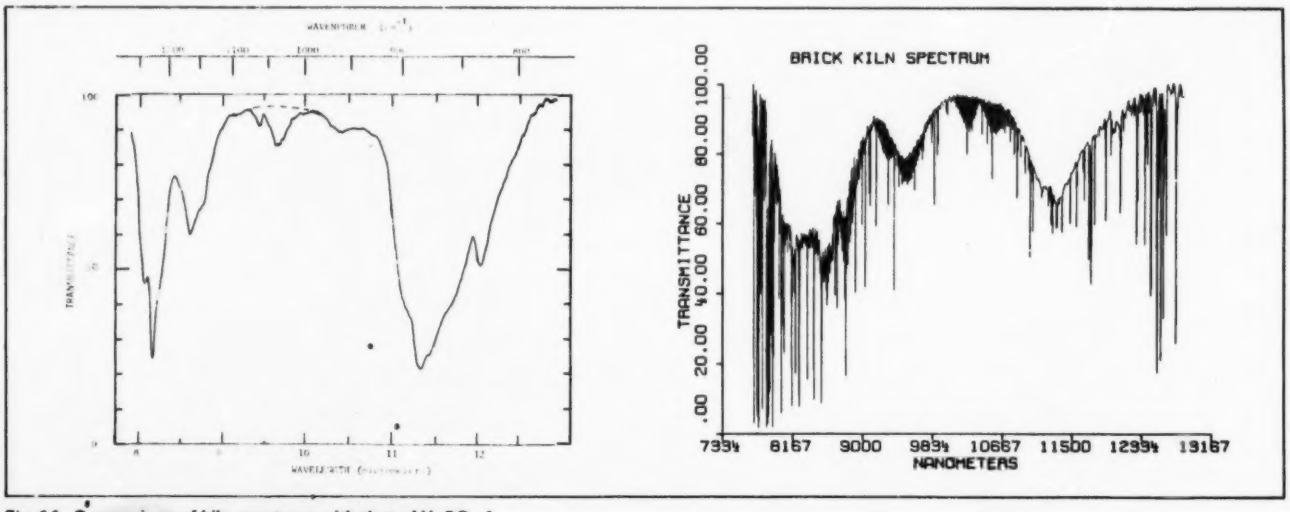

Fig. 11 Comparison of kiln spectrum with that of H_2SO_4.[8]

sufficient care, the results of the chemical method were within ±15% of the infrared method. Figure 15 shows the steps used in the analysis of the pond data (and are typical procedures used with longpath data). The clean air and pond spectra were both expressed in absorbance, and the strength of the H_2O line at 4174.67 cm^{-1} in the background spectrum was matched with that of the same line in the pond spectrum. The spectra were then subtracted to eliminate the effect of the weak H_2O line interference with the R(5) HF line. The HF concentration was determined to be 37 ppb.

V. SUMMARY

A commercial FT-IR system has been installed in a van and used to make air pollution measurements under a variety of conditions. The system is quite versatile and performance has not been affected by travel. The concentrations of many pollutants can be determined in the ppb range for a one kilometer path. It has been found valuable to generally collect spectra at a resolution of 0.125 cm^{-1}. This is sufficient to resolve essentially all spectral features which can be resolved at one atmosphere total pressure. Also, this resolution is needed for analysis of broadband features in order to minimize H_2O (or other) interferences.

Table I. Species Concentrations in Brick Kiln Emissions.

Species	ν (cm^{-1})	$K(\nu)$ (ppm meters)$^{-1}$	Reference for $K(\nu)$	C (ppm)
H_2SO_4	885	13 E-4	9	10
NO	1900	8.4 E-4	This work	5 7
CO	2176	3.9 E-3	This work	10
SO_2	2500	3.8 E-5	This work	95
HCl	2776	1.9 E-3	This work	6.5
HF	4174	*	5	40

*The HF concentration was calculated using the equivalent width method as described in Ref. 5.

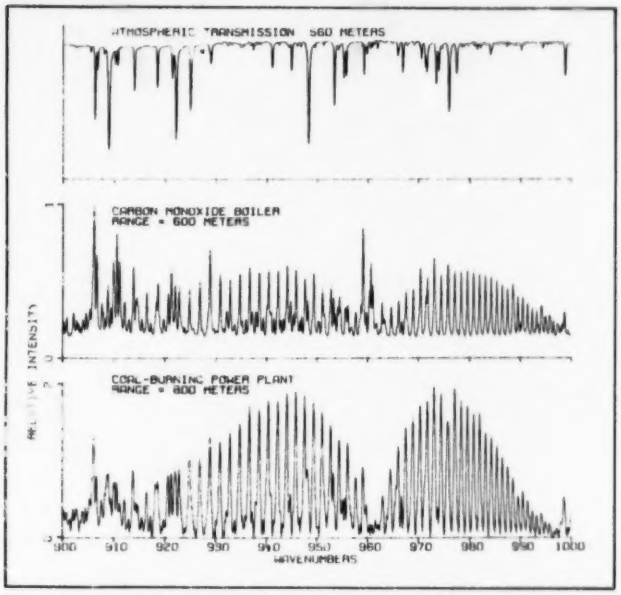
ATMOSPHERIC TRANSMISSION 560 METERS
CARBON MONOXIDE BOILER
RANGE = 600 METERS
COAL-BURNING POWER PLANT
RANGE = 600 METERS
RELATIVE INTENSITY
900 910 920 930 940 950 960 970 980 990 1000
WAVENUMBERS

Fig. 12. CO_2 emission spectra from industrial stack plumes.

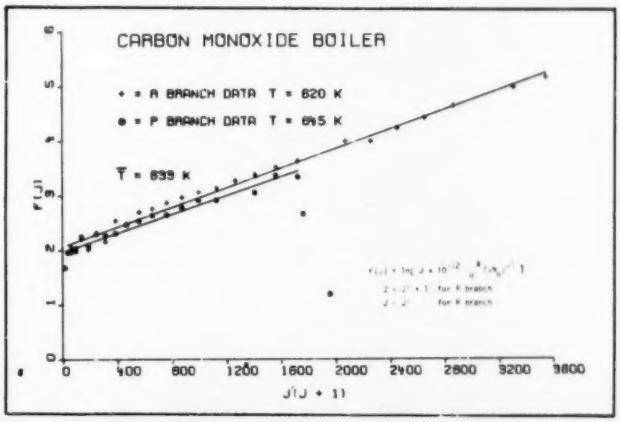

Fig. 13. Temperature plot for carbon monoxide boiler plume.

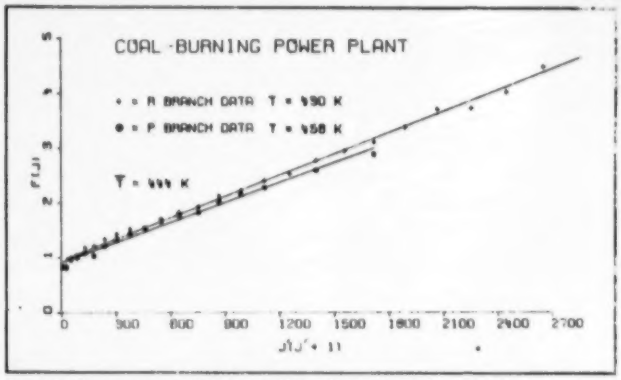

Fig. 14. Temperature plot for coal-burning power plant plume.

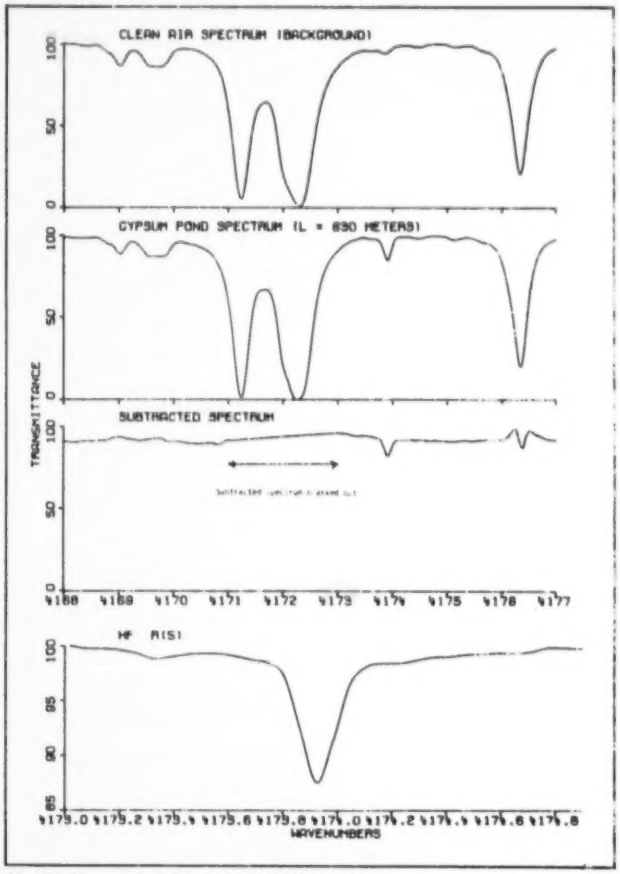

Fig. 15. Processing of gypsum pond spectra.

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